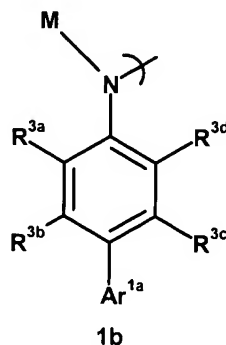
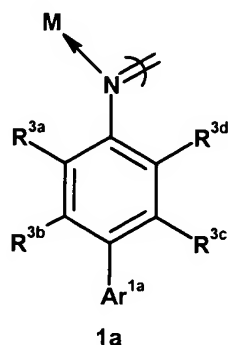


WE CLAIM:

1. A catalyst for olefin polymerization, comprising a Group 3-11 metal complex of a bidentate, tridentate, or tetradentate ligand, wherein said complex comprises at least one N-donor fragment of formula **1a** or **1b**;

5

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wherein:

15

M is a Group 3-11 transition metal;

$R^{3a-d}$  are each, independently, H, F, Cl, Br, hydrocarbyl, substituted hydrocarbyl, fluoroalkyl, nitro, heteroatom connected hydrocarbyl or heteroatom connected substituted hydrocarbyl; and

$Ar^{1a}$  is an aryl or heteroaryl group substituted at one or both ortho positions by a group  $Q^2$ ; wherein  $Q^2$  is hydrocarbyl, substituted hydrocarbyl, heteroatom connected hydrocarbyl or heteroatom connected substituted hydrocarbyl.

20

2. The catalyst according to Claim 1 wherein M is a Group 8-10 metal.

25

3. The catalyst according to Claim 2, wherein M is nickel, and  $Q^2$  is sufficiently long to extend sufficiently close to the metal M to increase the catalyst productivity at elevated temperatures, or in the presence of hydrogen, or both, relative to an otherwise similar catalyst wherein  $Q^2$  is replaced by H, Me, or Ph.

30

4. The catalyst according to Claim 2, wherein M is nickel, and  $Q^2$  is sufficiently long to extend sufficiently close to the metal M to increase the regioselectivity or stereoselectivity of comonomer incorporation, relative to an

otherwise similar catalyst wherein  $Q^2$  is replaced by H, Me, or Ph.

5. The catalyst according to Claim 2, wherein M is nickel, and  $Q^2$  is sufficiently long to extend sufficiently close to the metal M to decrease the amount of chain-running, relative to an otherwise similar catalyst wherein  $Q^2$  is replaced by H, Me, or Ph.

6. The catalyst according to Claim 2, wherein M is palladium, and  $Q^2$  is sufficiently long to extend sufficiently close to the metal M to decrease the amount of chain-running, relative to an otherwise similar catalyst wherein  $Q^2$  is replaced by H, Me, or Ph.

7. The catalyst according to Claim 2, wherein M is nickel, and  $Q^2$  is sufficiently long to extend sufficiently close to the metal M to increase the chain-running stereoselectivity, relative to an otherwise similar catalyst wherein  $Q^2$  is replaced by H, Me, or Ph.

8. The catalyst according to Claim 2, wherein M is nickel, and  $Q^2$  is sufficiently long to extend sufficiently close to the metal M to decrease the rate of activation of the catalyst when an alkylaluminum reagent is used as cocatalyst, relative to an otherwise similar catalyst wherein  $Q^2$  is replaced by H, Me, or Ph.

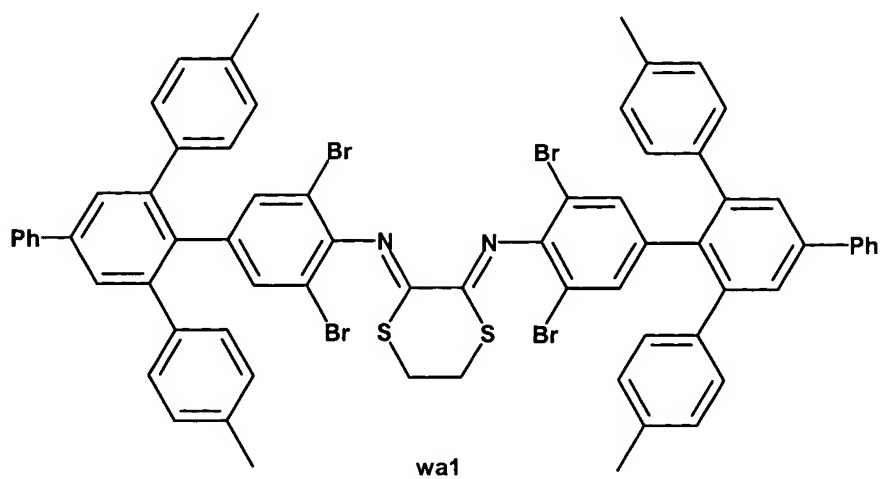
9. The catalyst according to Claim 2 which comprises a bidentate ligand selected from **Set 1**;

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Set 1

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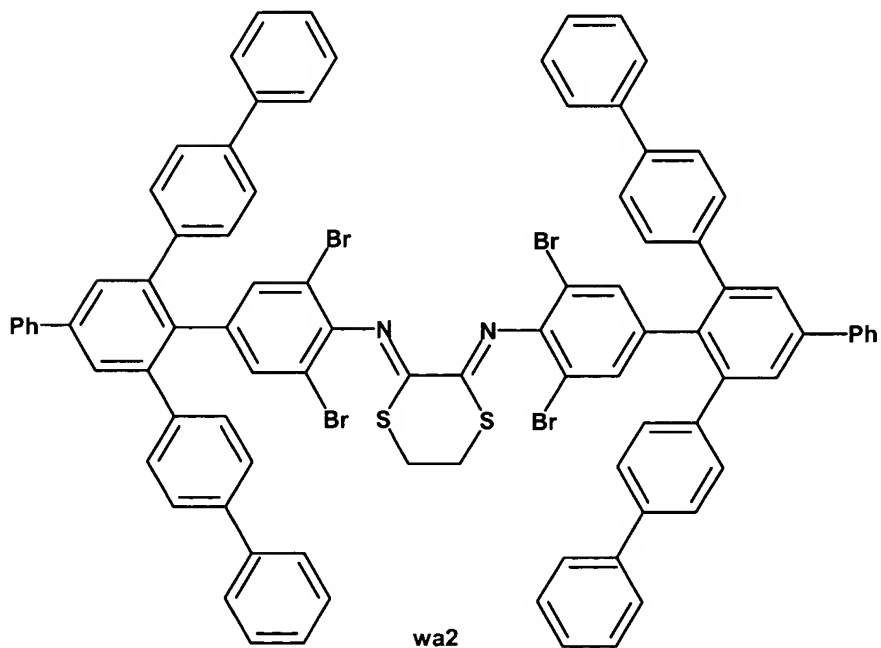
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Set 1, cont'd

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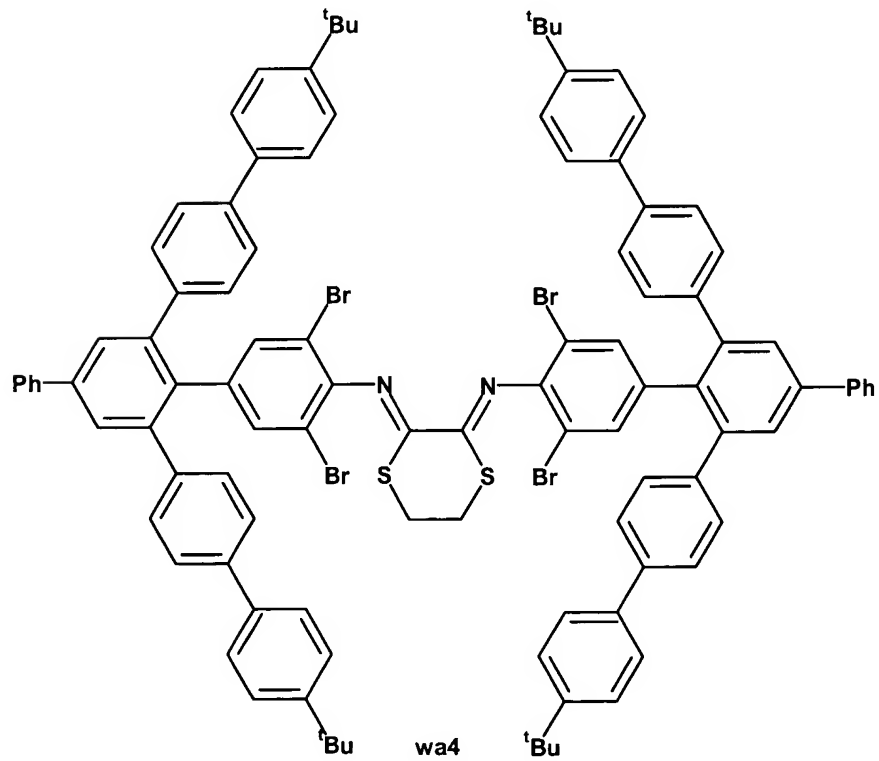
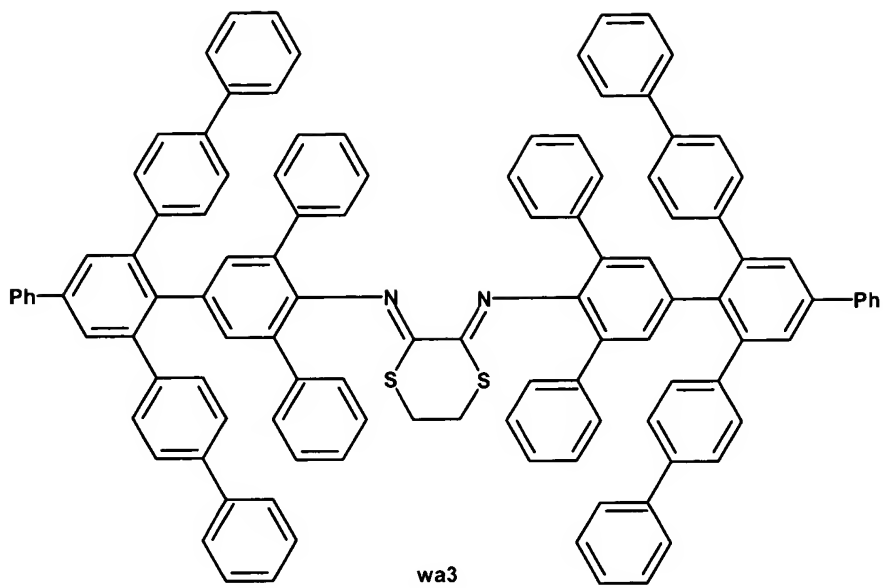
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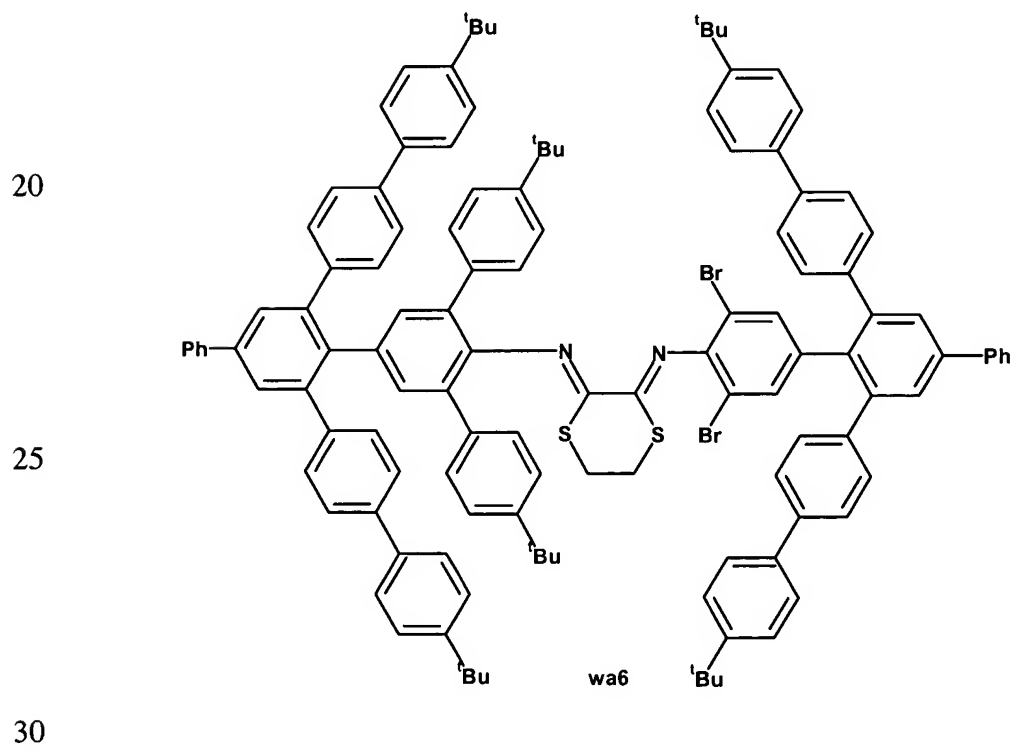
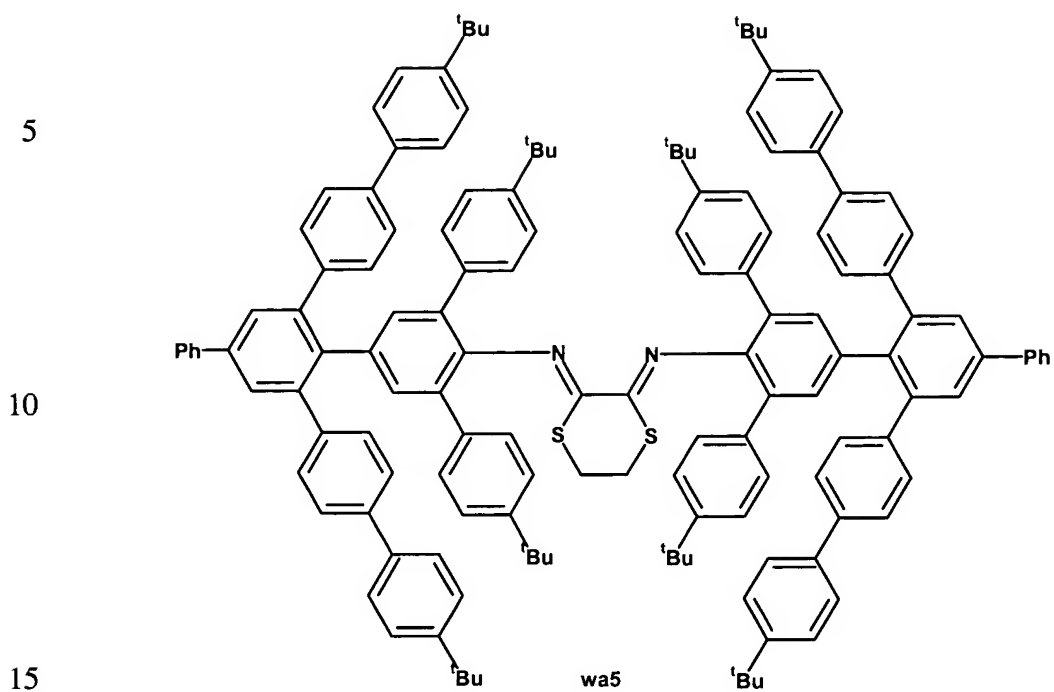
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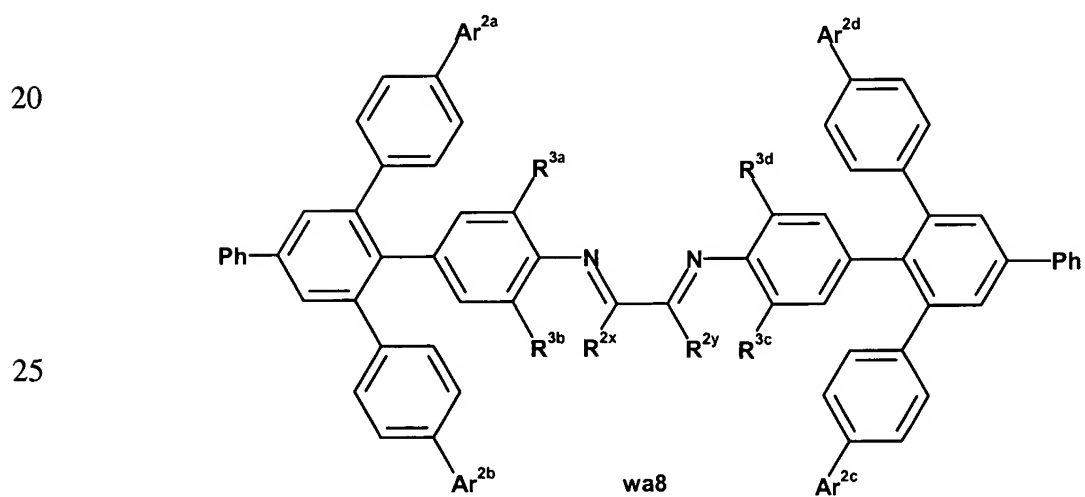
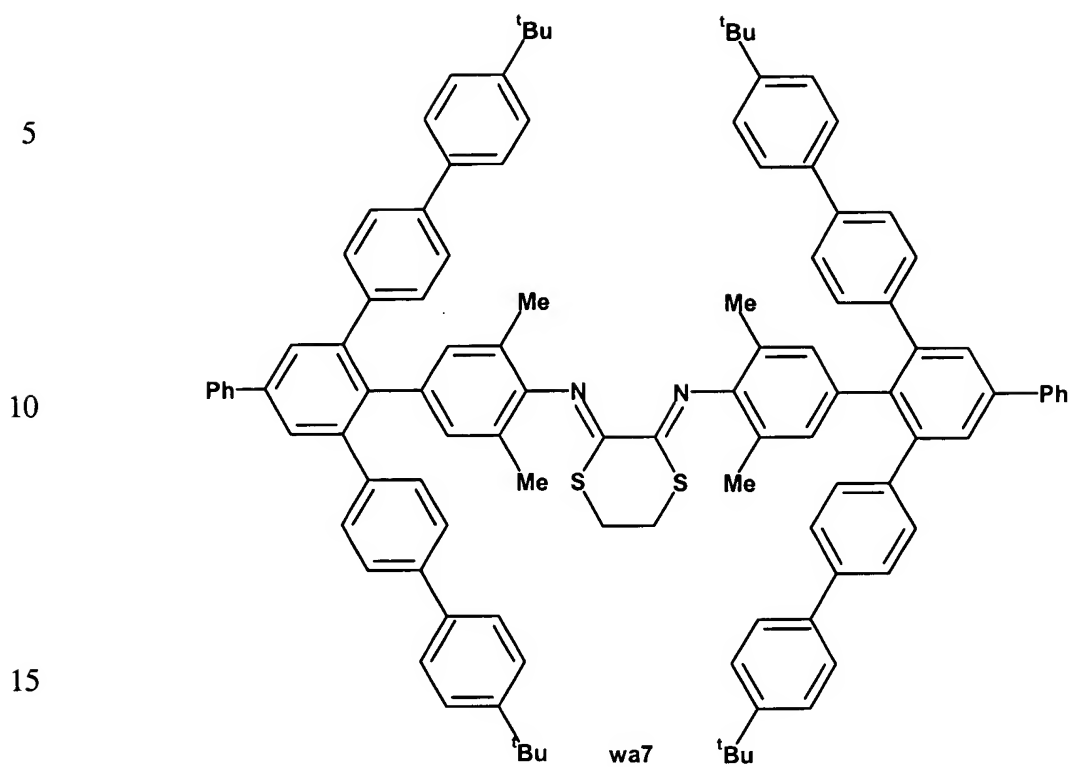
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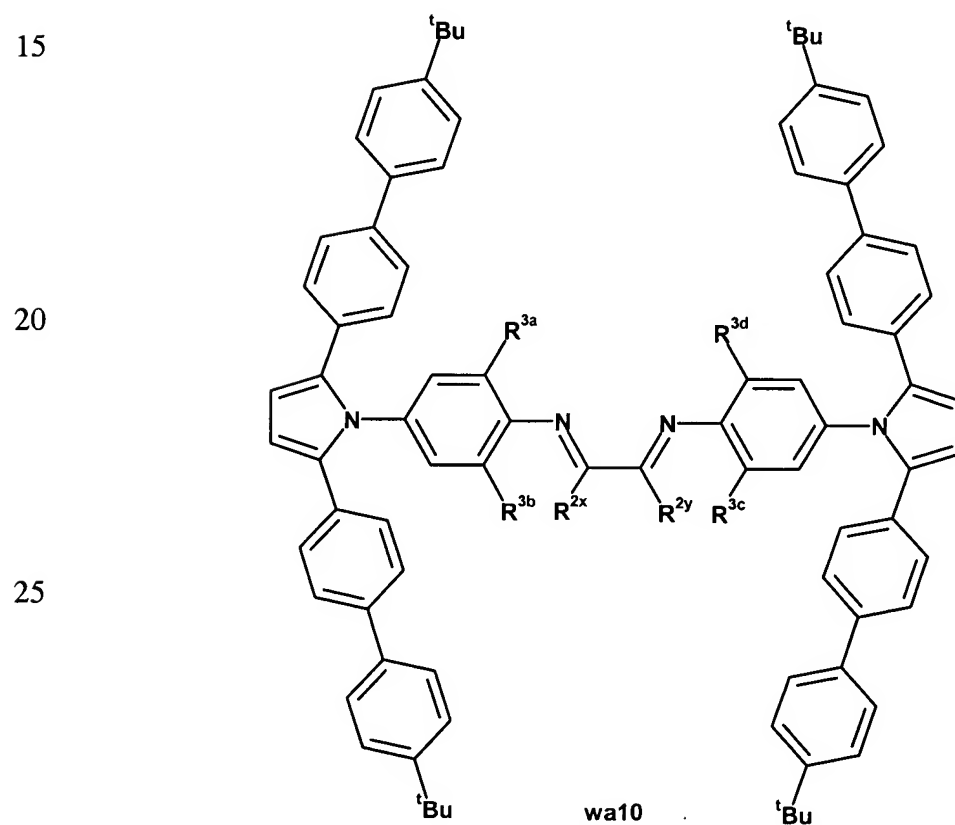
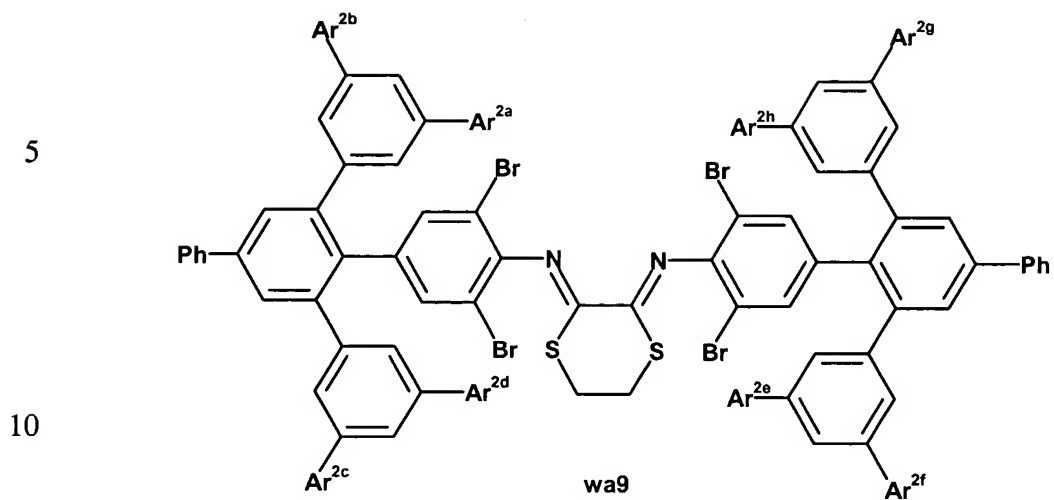
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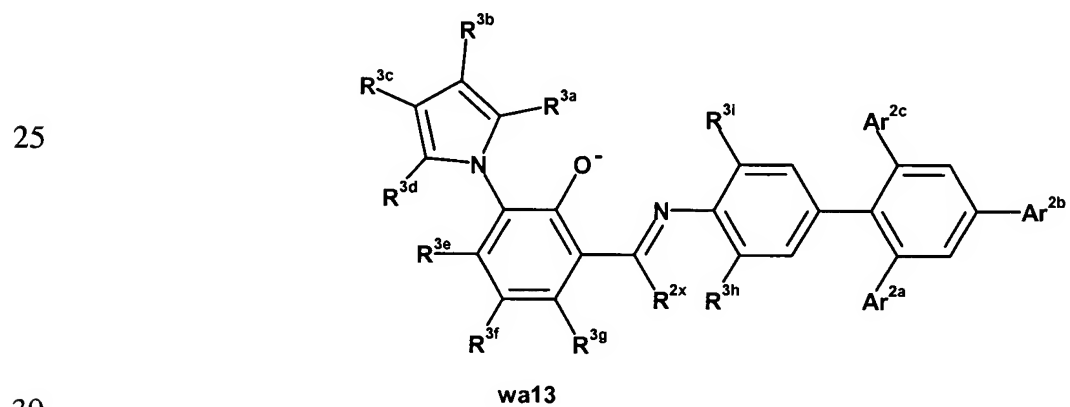
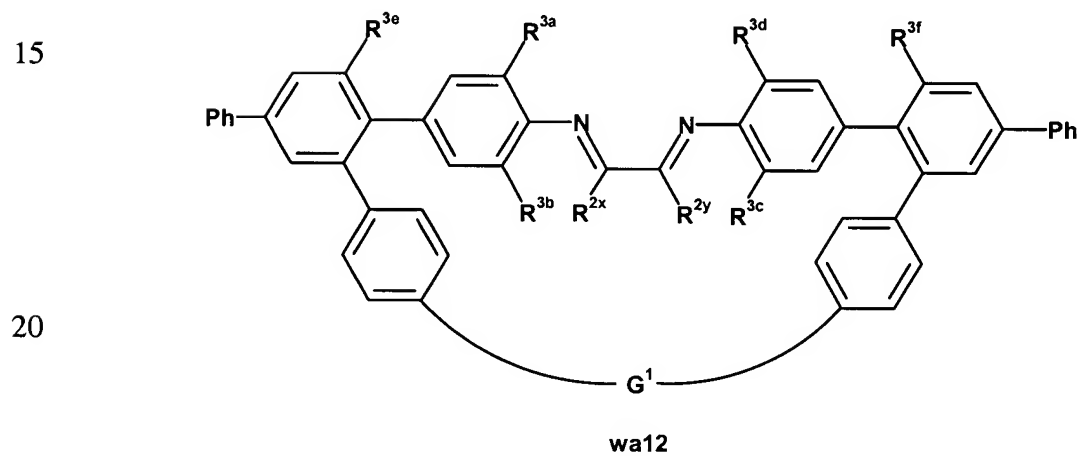
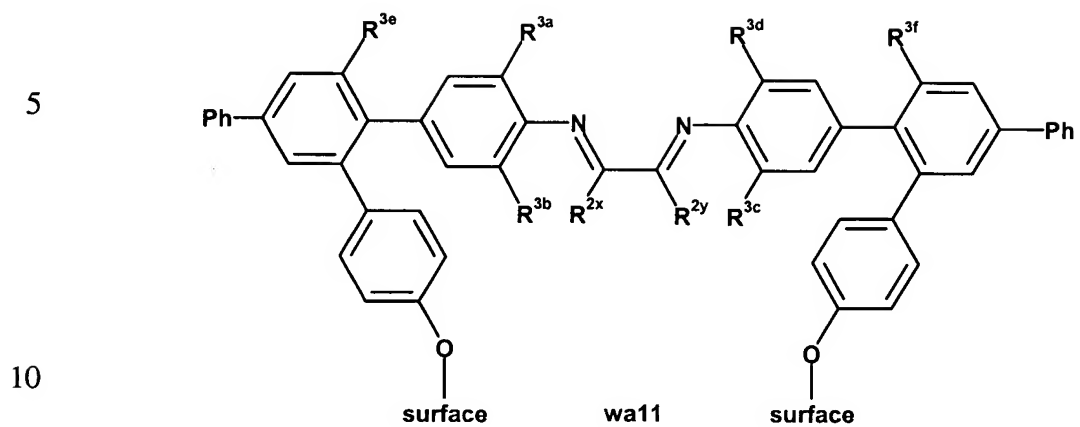
Set 1, cont'd



Set 1, cont'd



Set 1, cont'd

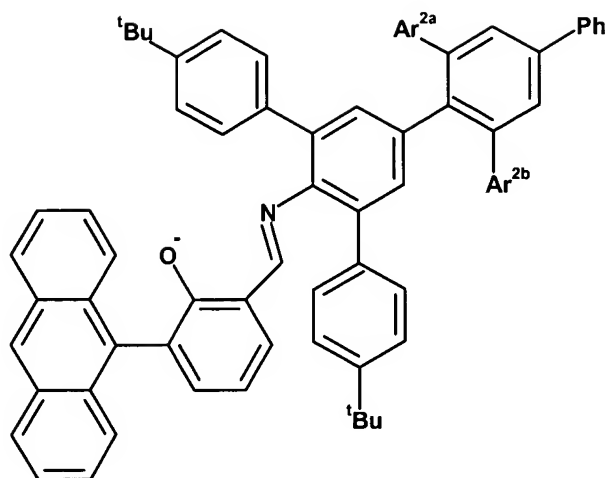




Set 1, cont'd

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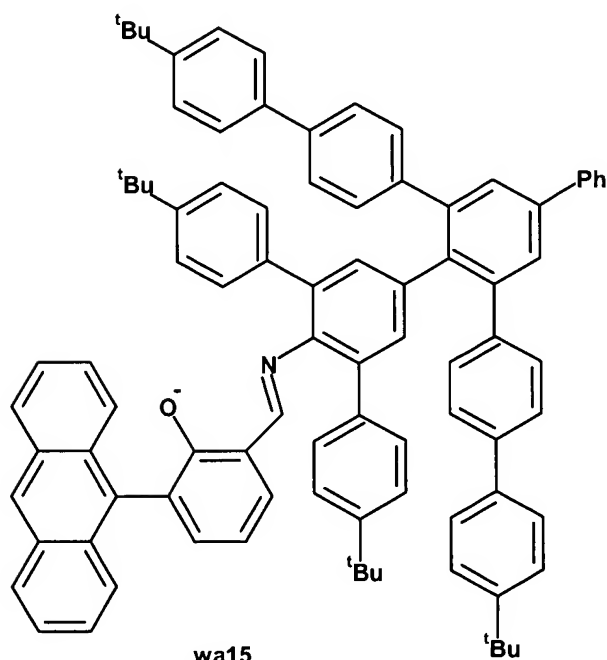


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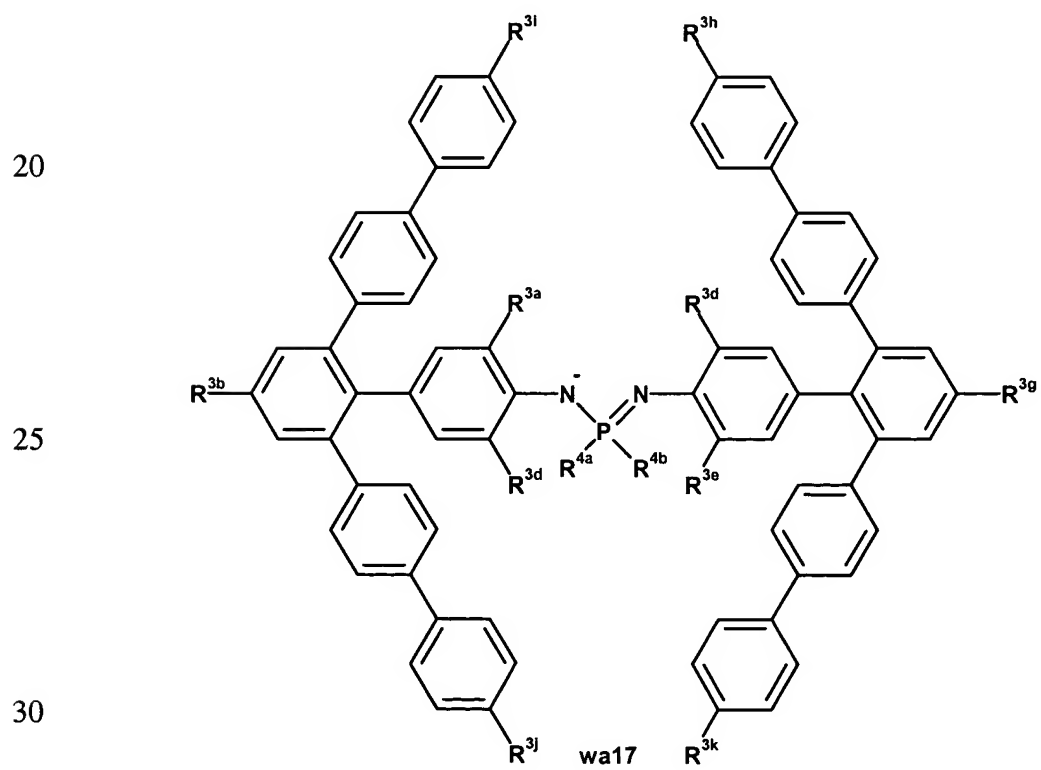
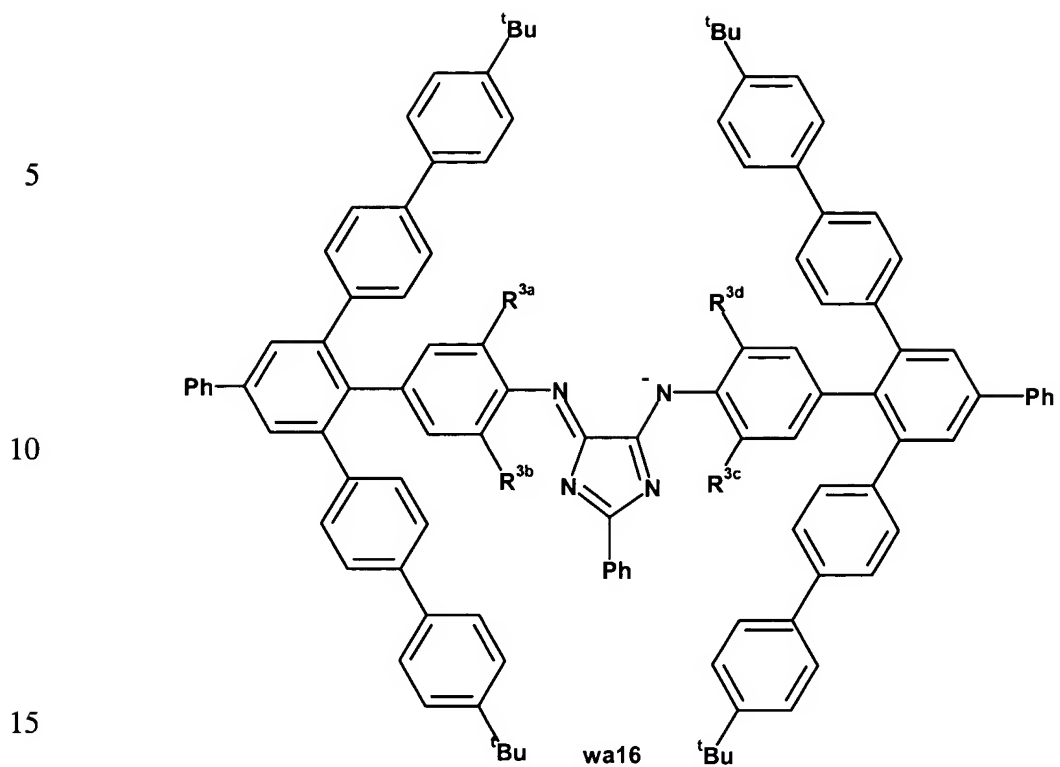
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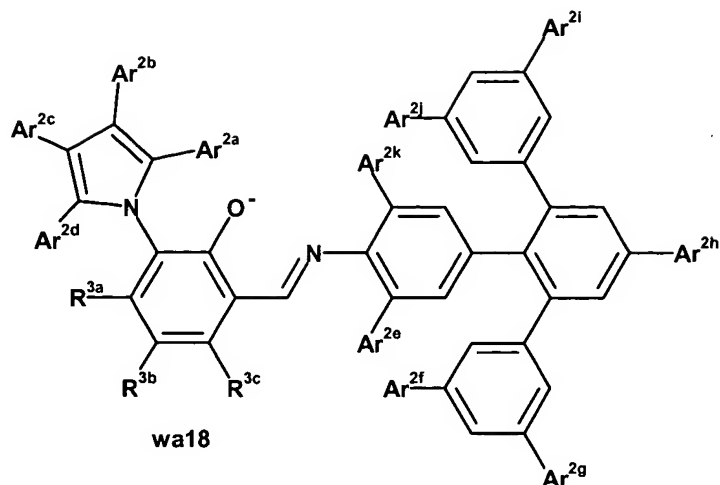
Set 1, cont'd



Set 1, cont'd

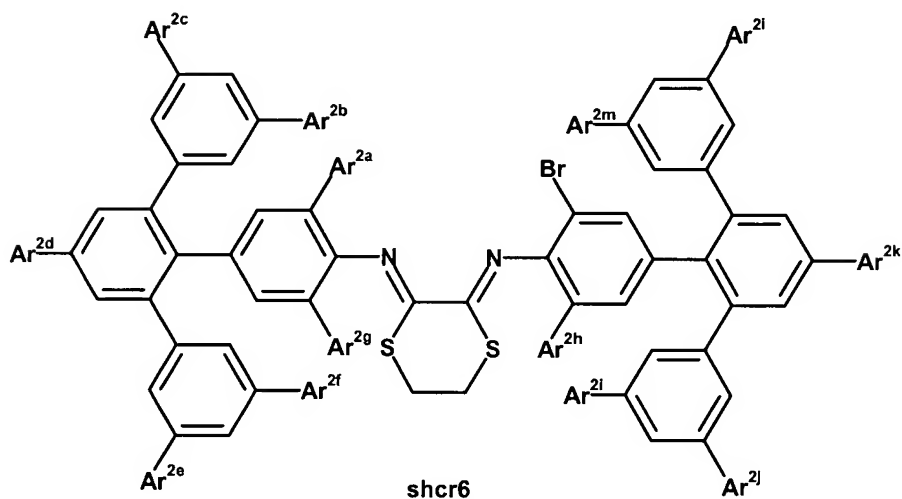
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wherein:

$R^{2x,y}$  are each independently H, hydrocarbyl, substituted hydrocarbyl, heteroatom connected hydrocarbyl, heteroatom connected substituted hydrocarbyl; silyl, or ferrocenyl; in addition,  $R^{2x}$  and  $R^{2y}$  may be linked by a bridging group;

30

$R^{3a-k}$  are each independently H, hydrocarbyl, substituted hydrocarbyl, heteroatom connected hydrocarbyl, heteroatom connected substituted hydrocarbyl, fluoroalkyl, silyl, boryl, fluoro, chloro, bromo, cyano, or nitro;

$R^{4a,b}$  are each independently hydrocarbyl, substituted hydrocarbyl, heteroatom connected hydrocarbyl, heteroatom connected substituted hydrocarbyl; in addition,  $R^{4a}$  and  $R^{4b}$  may be linked by a bridging group;

“surface” refers to a silicon or other atom which is part of, or attached to, a solid support;

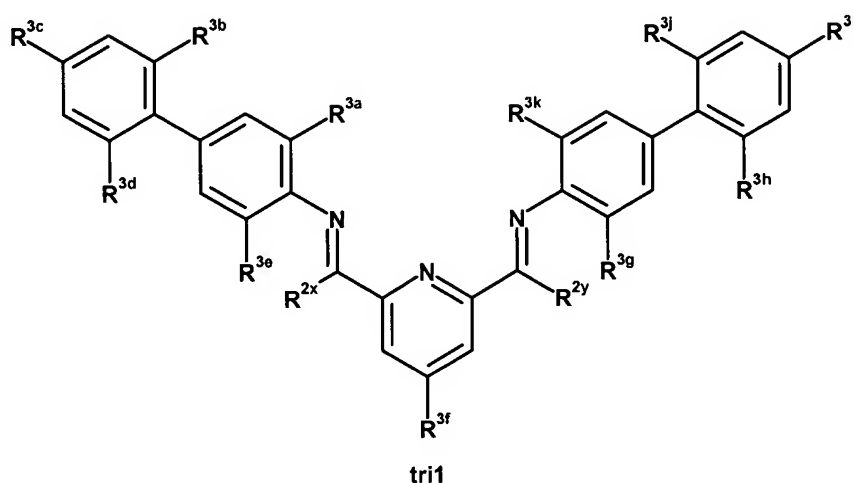
$G^1$  is a divalent bridging group; and

$Ar^{2a-m}$  are each independently hydrocarbyl, substituted hydrocarbyl, heteroatom attached hydrocarbyl, heteroatom attached substituted hydrocarbyl, halo, nitro, boryl, or trialkoxysilane.

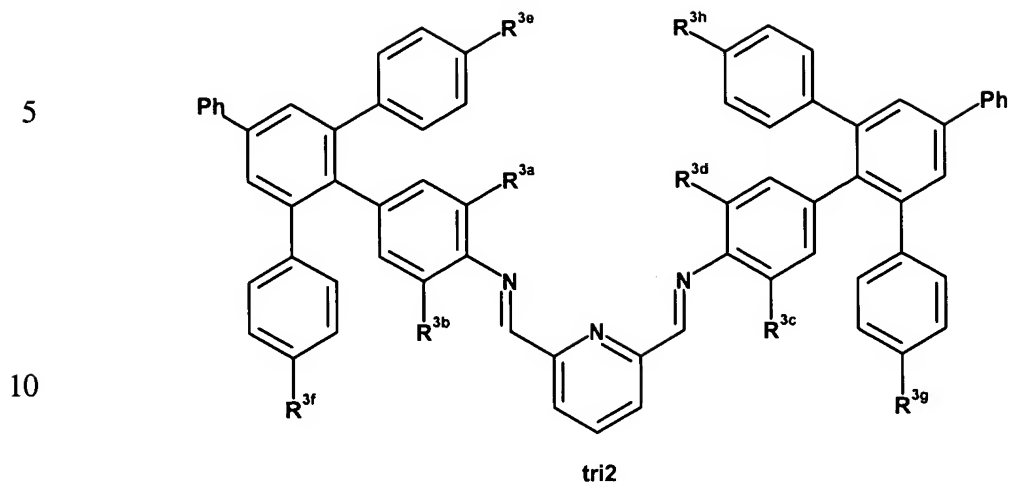
10. The catalyst according to Claim 2, wherein M is iron or cobalt, the catalyst comprises a tridentate ligand, and  $Q^2$  which is sufficiently long to extend sufficiently close to the metal M to increase the catalyst productivity at elevated temperatures.

11. The catalyst according to Claim 10, wherein said tridentate ligand is selected from Set 2;

# Set 2



Set 2, cont'd



wherein:

15  $R^{2x,y}$  are each independently H, hydrocarbyl, substituted hydrocarbyl, heteroatom connected hydrocarbyl, heteroatom connected substituted hydrocarbyl; silyl, or ferrocenyl; and

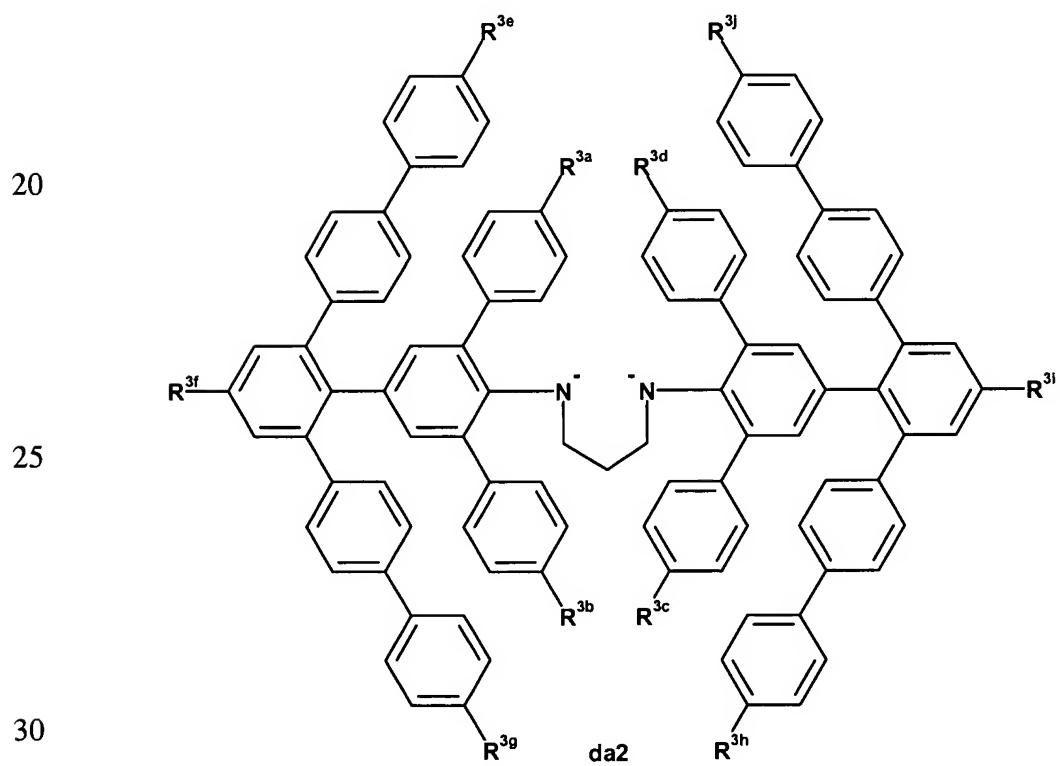
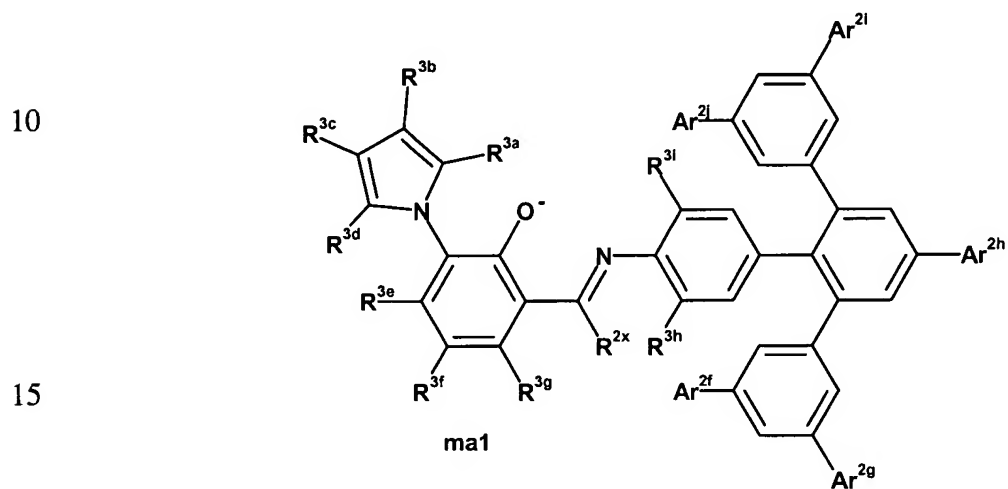
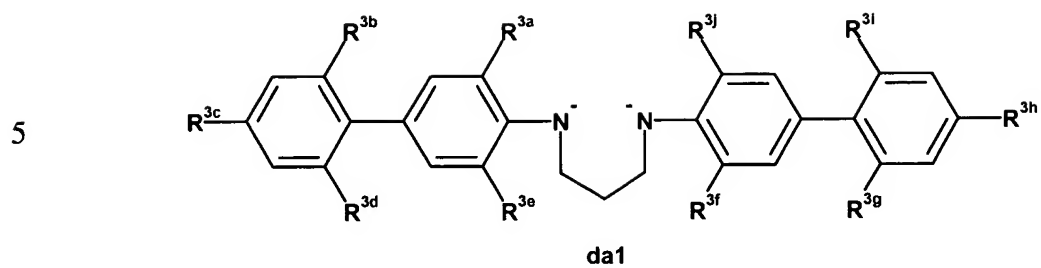
$R^{3a-k}$  are each independently H, hydrocarbyl, substituted hydrocarbyl, heteroatom connected hydrocarbyl, heteroatom connected substituted hydrocarbyl, 20 fluoroalkyl, silyl, boryl, fluoro, chloro, bromo, cyano, or nitro.

12. The catalyst according to Claim 1, comprising a titanium or zirconium complex of a bidentate ligand selected from Set 3;

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Set 3



wherein:

$R^{2x}$  is H, hydrocarbyl, substituted hydrocarbyl, heteroatom connected hydrocarbyl, heteroatom connected substituted hydrocarbyl; silyl, or ferrocenyl;

$R^{3a-j}$  are each independently H, hydrocarbyl, substituted hydrocarbyl,  
5 heteroatom connected hydrocarbyl, heteroatom connected substituted hydrocarbyl, fluoroalkyl, fluoro, chloro, or bromo; and

$Ar^{2a-j}$  are each independently hydrocarbyl, substituted hydrocarbyl, heteroatom attached hydrocarbyl, heteroatom attached substituted hydrocarbyl, halo, nitro, boryl, or trialkoxysilane.

10

13. The catalyst according to Claim 1, further comprising a solid support.

14. The catalyst according to Claim 13, which is attached to the solid support via a covalent bond to the group  $Ar^{1a}$ .

15

15. A process for the polymerization of olefins, comprising contacting one or more olefins with the catalyst of Claim 1.

16. The process according to Claim 15, wherein at least one of said  
20 olefins is ethylene.

17. The process according to Claim 15, wherein the olefin is ethylene, M is nickel, the temperature is at least 80 °C, the pressure is less than about 800 psig, sufficient hydrogen is added to reduce the number average molecular weight of the  
25 polymer by at least 20% relative to an otherwise similar reaction conducted in the absence of hydrogen, the catalyst productivity is at least 500 kg polyethylene per g nickel, and the polymer has a DSC first cycle peak melting point greater than 131 °C.

18. The process according to Claim 17, wherein sufficient hydrogen is added to reduce the number average molecular weight of the polymer by at least 50% relative to an otherwise similar reaction conducted in the absence of hydrogen,

and the polymer has a DSC first cycle peak melting point greater than 133 °C.

19. The process according to Claim 15, wherein at least one of the olefins is ethylene, M is palladium and the amount of chain running is reduced.

20. A bidentate, tridentate, or tetradentate ligand of Set 1, Set 2, or Set 3.

21. A process for the polymerization of olefins, comprising contacting one or more olefins with a catalyst comprising a Group 8-10 metal complex of a bidentate, N,N-donor ligand, wherein the first of said donor nitrogens, N<sup>1</sup>, is substituted by an aromatic or heteroaromatic ring wherein the ortho substituents are aryl or heteroaryl groups, and the second of said donor nitrogens, N<sup>2</sup>, is substituted by an aromatic or heteroaromatic ring wherein one or both of the ortho substituents are other than aryl or heteroaryl; wherein said catalyst is capable of homopolymerizing ethylene to produce a polymer with a number average molecular weight of at least 20,000 g/mole and at least 20 branch points per 1000 carbons with a catalyst productivity of at least 500 kg polyethylene per g of Group 8-10 metal at a temperature of at least 60 °C at a partial pressure of ethylene of at least 350 psia at a partial pressure of hydrogen of at least 2 psia.

22. The process according to Claim 21, wherein said ligand is such that the calculated rate of olefin rotation in square planar complexes of the type (L)M(H)(R<sup>1a</sup>CH=CHR<sup>1b</sup>)<sup>n+</sup>, wherein n = 0 or 1, M is nickel or palladium, L is said bidentate, N,N-donor ligand, R<sup>1a</sup> is H or Me, and R<sup>1b</sup> is Me, and R<sup>1a</sup>CH=CHR<sup>1b</sup> is trans to N<sup>1</sup>, is at least 2 times higher than the calculated rate of olefin rotation in the complex wherein R<sup>1a</sup>CH=CHR<sup>1b</sup> is cis to N<sup>1</sup>.

23. The process according to Claim 22, wherein the calculated rate of olefin rotation in the complex wherein R<sup>1a</sup>CH=CHR<sup>1b</sup> is trans to N<sup>1</sup> is at least 4 times higher than the calculated rate of olefin rotation in the complex wherein



$R^{1a}CH=CHR^{1b}$  is cis to  $N^1$ .

24. The process according to Claim 21, wherein the metal is nickel,  $N^1$  is substituted by a 2,6-diaryl substituted aryl group or a 2,5-diaryl substituted 1-  
5 pyrrolyl group, and  $N^2$  is substituted by an aromatic or heteroaromatic ring wherein one or both of the ortho substituents are other than aryl or heteroaryl.

25. The process according to Claim 24, wherein  $N^1$  is substituted by a 2,6-diaryl substituted aryl group,  $N^2$  is substituted by an aromatic ring wherein one  
10 or both of the ortho substituents are other than aryl or heteroaryl, and the catalyst productivity is at least 500 kg polyethylene per g nickel at a temperature of at least 70 °C.

26. The process according to Claim 25, wherein  $N^2$  is substituted by an  
15 aromatic ring wherein one of the ortho substituents is aryl, heteroaryl or bromo, and the other ortho substituent is bromo.

27. The process according to Claim 21, wherein the bidentate ligand is selected from **Set 4**;

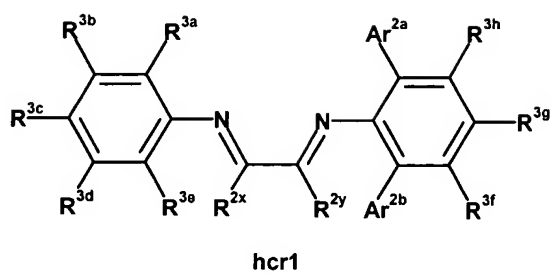
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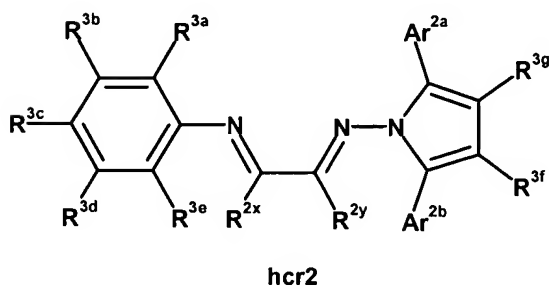
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Set 4

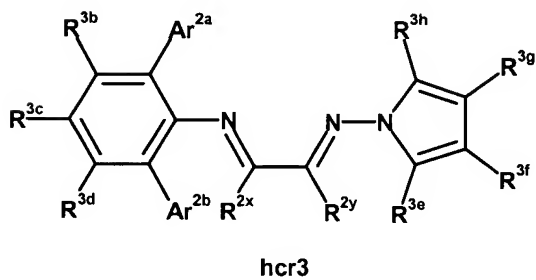
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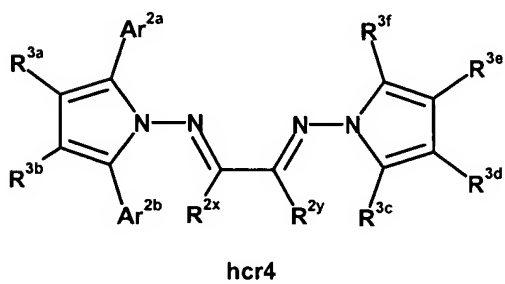


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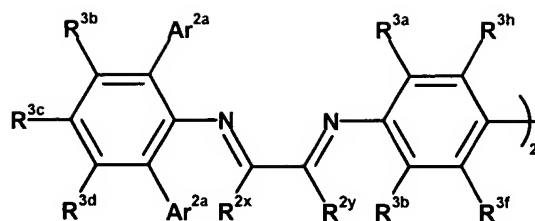
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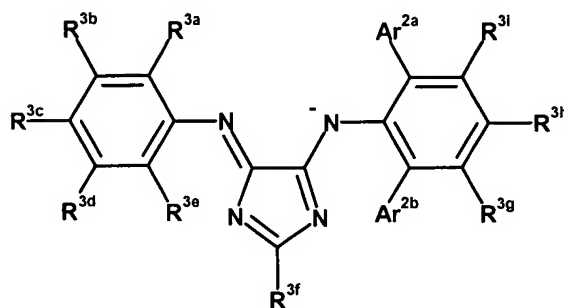
Set 4, cont'd

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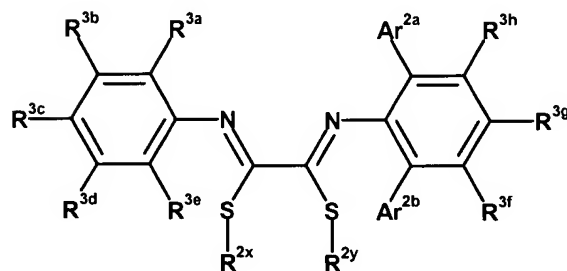
hcr5

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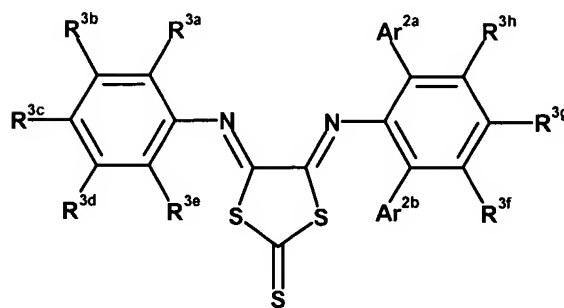
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hcr7

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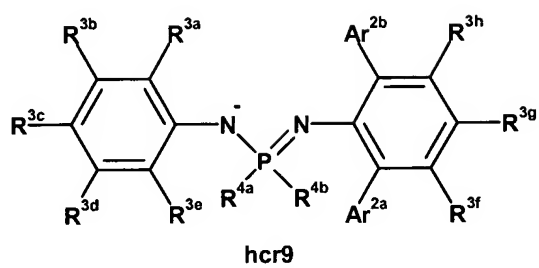
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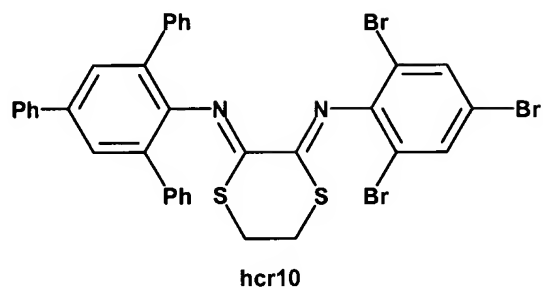
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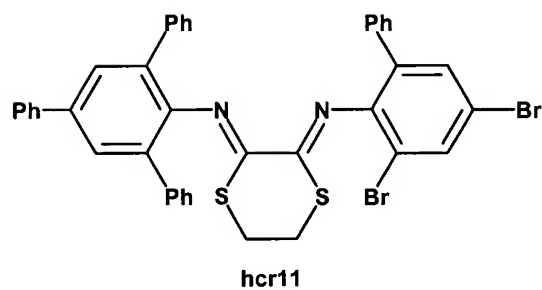
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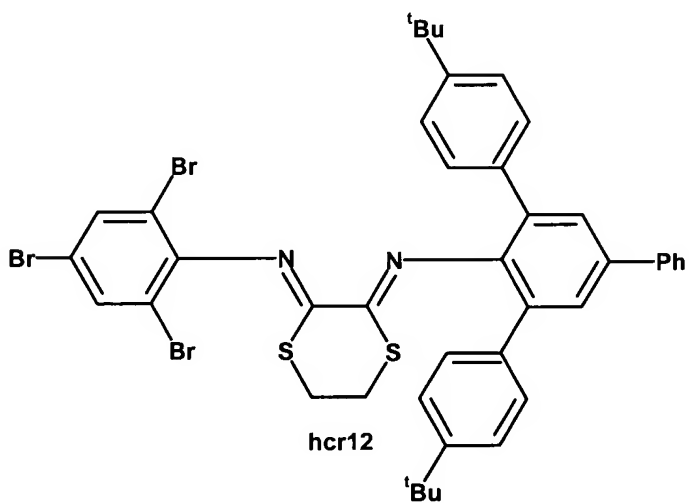


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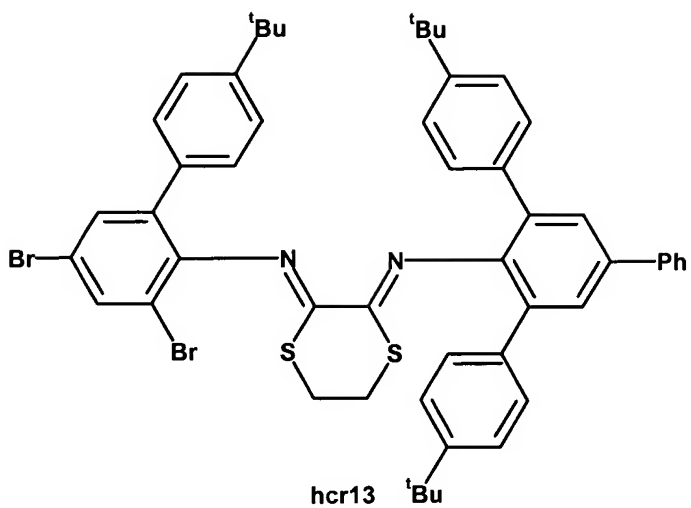
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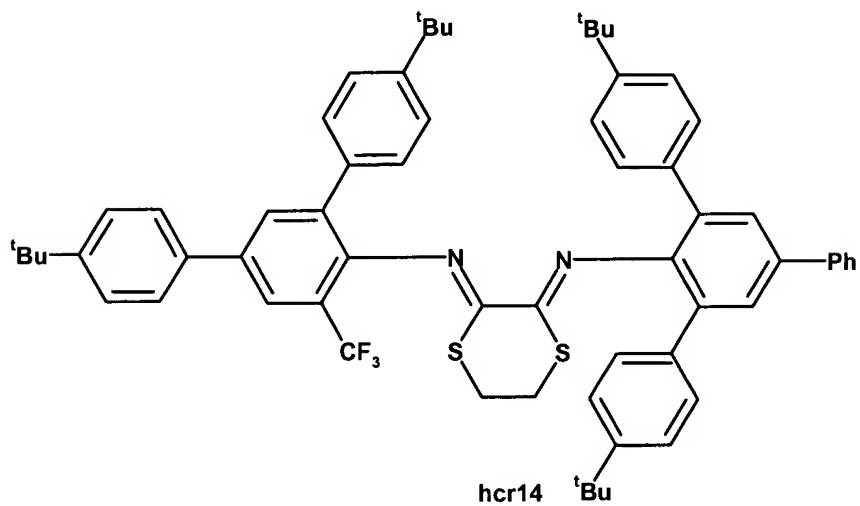
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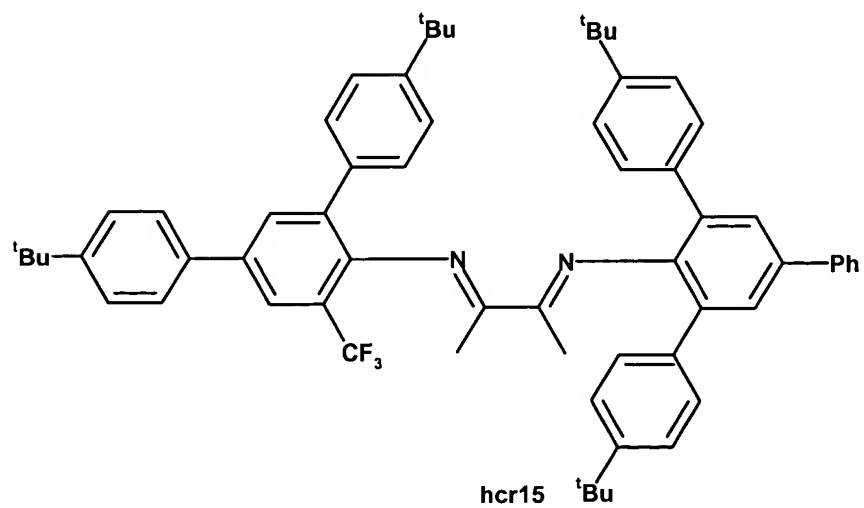
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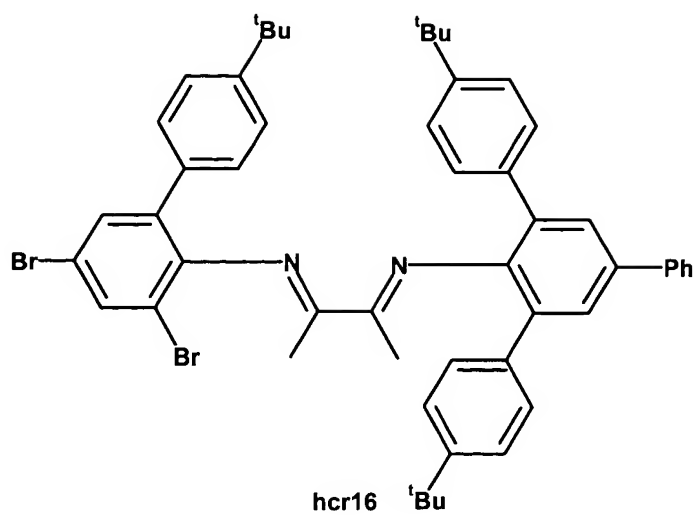


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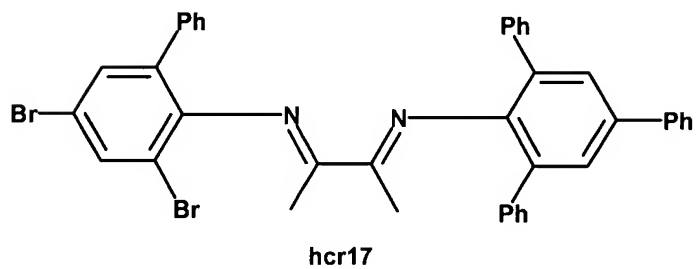
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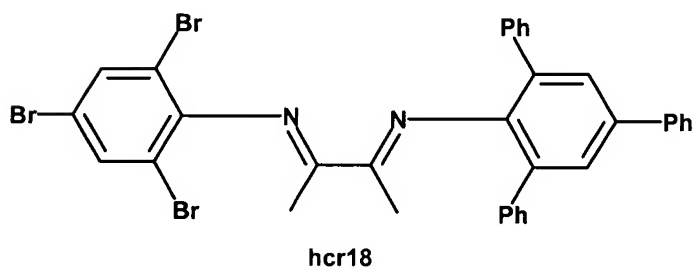


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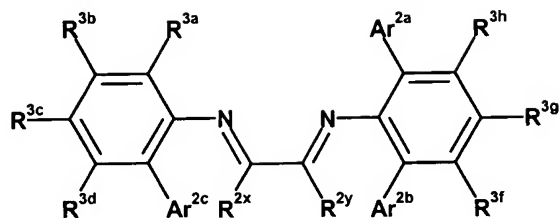
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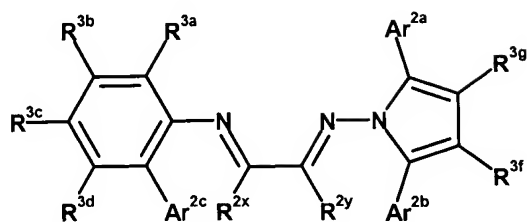
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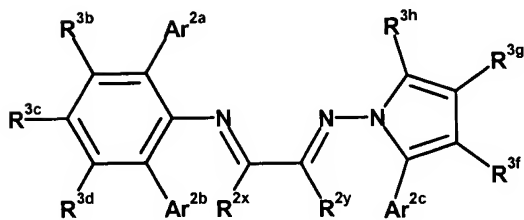
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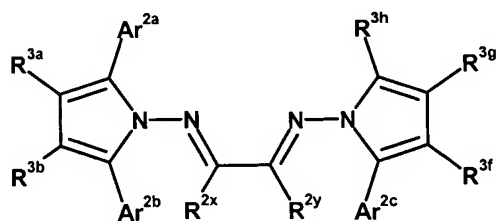
shcr2

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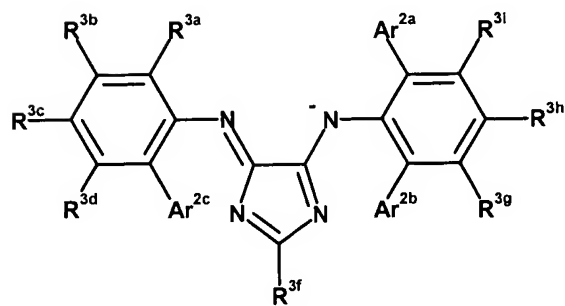
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shcr4

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shcr5

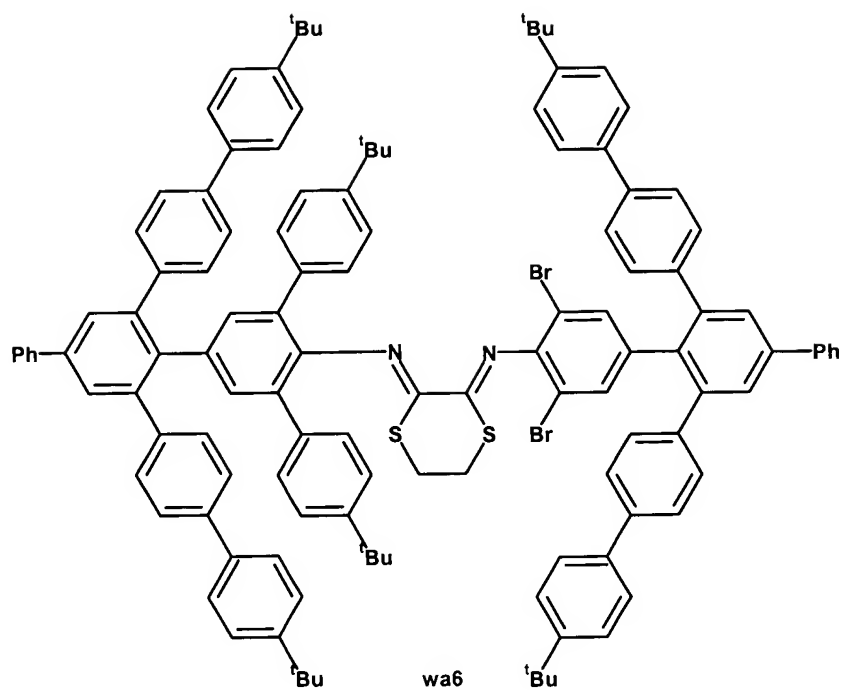
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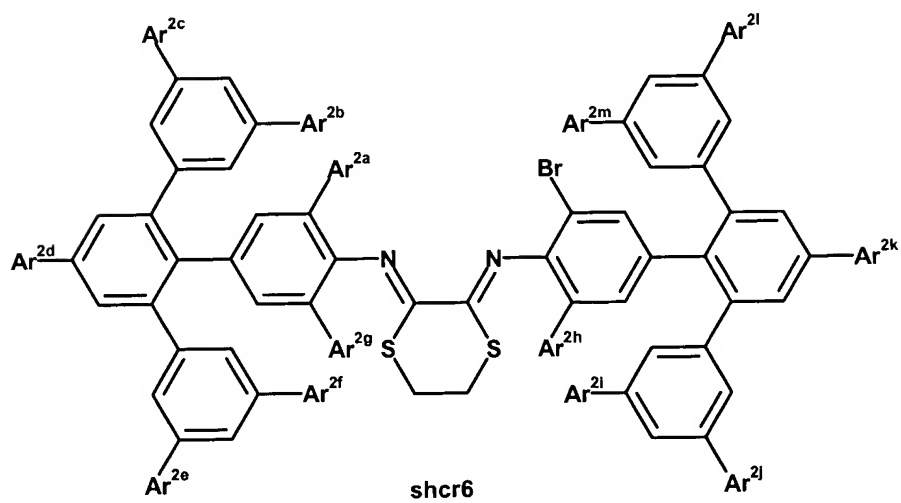
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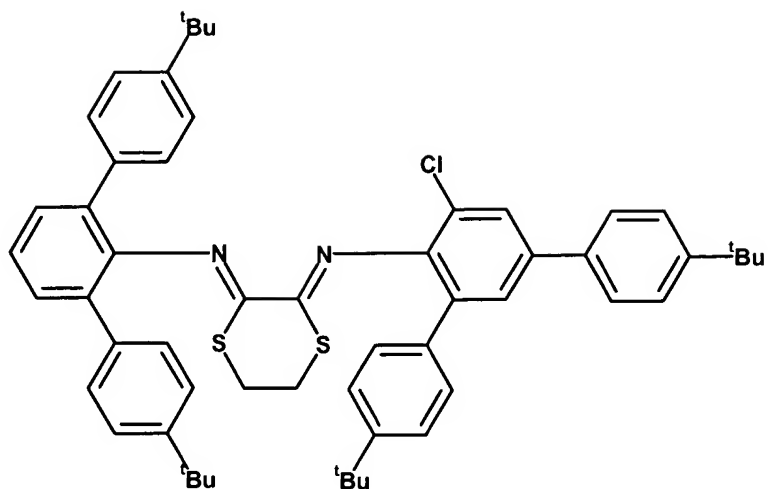
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Set 4, cont'd

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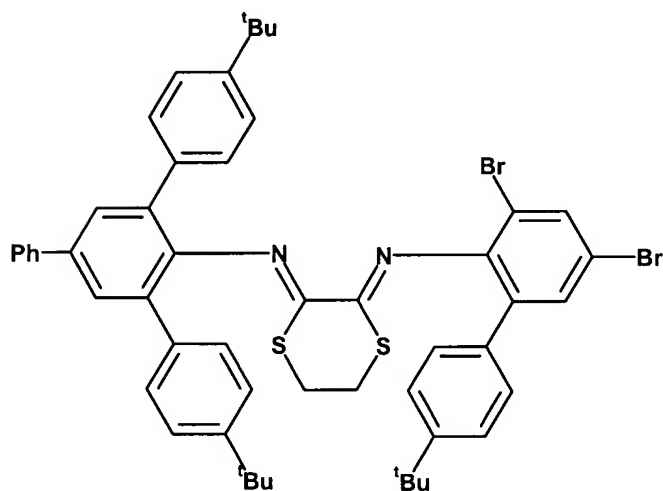
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shcr7

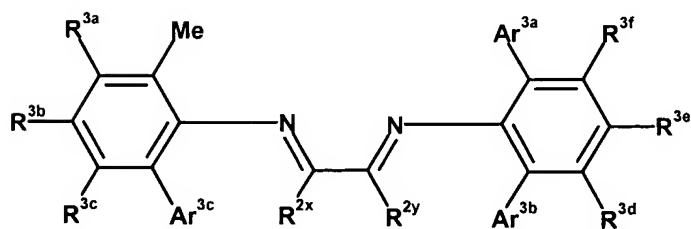
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shcr8

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shcr9

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wherein:

$R^{2x,y}$  are each independently H, hydrocarbyl, substituted hydrocarbyl, heteroatom connected hydrocarbyl, heteroatom connected substituted hydrocarbyl; silyl, or ferrocenyl; in addition,  $R^{2x}$  and  $R^{2y}$  may be linked by a bridging group;

5  $R^{3a-i}$  are each independently H, hydrocarbyl, substituted hydrocarbyl, heteroatom connected hydrocarbyl, heteroatom connected substituted hydrocarbyl, fluoroalkyl, silyl, boryl, fluoro, chloro, bromo, cyano, or nitro;

$Ar^{2a-m}$  are each independently aryl or heteroaryl; and

10  $Ar^{3a-c}$  are each independently 4-substituted aryl groups; wherein the 4-substituents are selected from the group consisting of hydrocarbyl, substituted hydrocarbyl, heteroatom connected hydrocarbyl, heteroatom connected substituted hydrocarbyl, fluoroalkyl, silyl, boryl, fluoro, chloro, bromo, cyano, phenylsulfonyl, and nitro.

15 28. A polymer prepared according to the process of Claim 21.

29. The process according to Claim 21 wherein the olefin is ethylene and the polymer is an ethylene homopolymer wherein the average spacing between branch points is such that there is at least a 10% excess of sequences of the type  
20  $-CHR-(CH_2)_{4n+2}-CHR-$ , where R is alkyl and n is 0 or a positive integer, relative to sequences of the type  $-CHR-(CH_2)_{2m}-CHR-$ , where R is alkyl and m is a positive integer.

30. The process according to Claim 21 wherein the olefin is ethylene,  $N^2$   
25 is substituted by a 2-aryl-6-bromo-aryl group and the polymer is an ethylene homopolymer wherein there is an excess of isotactic sequences of the type  $-CHR^{1a}-(CH_2)_{4n+2}-CHR^{1b}-$ , where  $R^{1a}$  and  $R^{1b}$  are hydrocarbyl or substituted hydrocarbyl branches and n is 0 or 1, relative to a random distribution.

30 31. A process for the polymerization of olefins, comprising contacting one or more olefins with a catalyst comprising a Group 8-10 metal complex of a bidentate, tridentate or multidentate ligand, wherein said catalyst is activated using

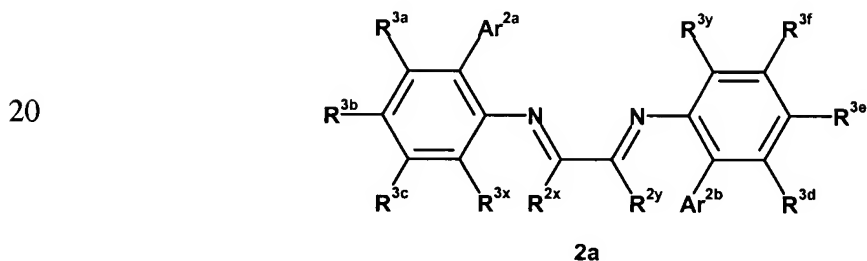
an alkylaluminum compound, wherein said alkylaluminum compound is subsequently selectively deactivated before the bulk of said polymerization has occurred.

5            32.     The process according to Claim 31, wherein said alkylaluminum compound is selectively deactivated through the addition of a phenol or substituted phenol.

             33.     The process according to Claim 31, wherein said Group 8-10 metal  
10     complex is a cationic nickel complex of a bidentate N,N-donor ligand.

             34.     The process according to Claim 31, wherein said Group 8-10 metal complex is a cationic iron or cobalt complex of a tridentate ligand.

15            35.     A catalyst for the polymerization of olefins, comprising a nickel complex of a ligand of formula **2a**;



wherein:

25            R<sup>2x,y</sup> are each independently hydrocarbyl, substituted hydrocarbyl, heteroatom connected hydrocarbyl, heteroatom connected substituted hydrocarbyl, or silyl; in addition, R<sup>2x</sup> and R<sup>2y</sup> may be linked by a bridging group;

             R<sup>3a-f</sup> are each independently H, hydrocarbyl, substituted hydrocarbyl, heteroatom connected hydrocarbyl, heteroatom connected substituted hydrocarbyl,  
30     fluoroalkyl, silyl, boryl, fluoro, chloro, bromo, iodo, cyano, or nitro;

             R<sup>3x,y</sup> are each independently halo or fluoroalkyl; and

Ar<sup>2a,b</sup> are each independently aryl or heteroaryl.

36. The catalyst according to Claim 35, wherein R<sup>2x</sup> and R<sup>2y</sup> are linked by a bridging group.

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37. A process for the polymerization of olefins comprising contacting ethylene and optionally other olefins with the catalyst of Claim 35 in the presence of sufficient hydrogen to reduce the number average molecular weight of the polymer by at least 10% relative to an otherwise similar process carried out in the absence of hydrogen.

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38. An ethylene homopolymer having a number average molecular weight of at least 10,000 g/mole, total branching of less than about 70 branches per 1000 carbons, at least 10% saturated hydrocarbon polymer chains, and a ratio of C<sub>5</sub> and longer branches to methyl branches of at least 0.35.

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39. The homopolymer according to Claim 38, wherein the total branching is less than about 60 branches per 1000 carbons; at least 25% of the polymer chains are saturated hydrocarbon chains; and the ratio of C<sub>5</sub> and longer branches to methyl branches is at least 0.40.

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40. The homopolymer according to Claim 38, wherein the total branching is less than about 60 branches per 1000 carbons; and the ratio of C<sub>5</sub> and longer branches to methyl branches is at least 0.45.

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41. The homopolymer according to Claim 38, having a DSC curve that shows a bimodal melt endotherm on a second heat from the melt, with the area of the smaller of the two peaks representing at least 25% of the total melt endotherm.

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